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$Nb_2Cl_{10}(P_4S_{10})_2$: A Co-Crystal of Nb_2Cl_{10} and P_4S_{10}

Arno Pfitzner* and Diana Hoppe

Regensburg, Institut für Anorganische Chemie der Universität

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Dedicated to Professor Hans Georg von Schnering on the Occasion of his 75th Birthday

Abstract. Red moisture−sensitive crystals of $Nb_2Cl_{10}(P_4S_{10})_2$ were obtained from a solution of P_4S_{10} and Nb_2Cl_{10} in CS_2. $Nb_2Cl_{10}(P_4S_{10})_2$ crystallises in the space group $P\bar{1}$ with a = 9.577(2), b = 10.894(2), c = 11.477(2) Å, α = 71.40(1), β = 68.14(1), γ = 67.58(1)°; V = 1005.2(3) Å^3, Z = 2. In the crystal structure molecules of P_4S_{10} and Nb_2Cl_{10} are arranged similar to the packing of the ions in the CaF_2 structure type. A comparison of the Raman spectrum of $Nb_2Cl_{10}(P_4S_{10})_2$ with spectra of the corresponding reactants indicates that no significant bonds are present between both components of the title compound. Therefore, $Nb_2Cl_{10}(P_4S_{10})_2$ has to be considered as a co-crystal of the starting materials. $Ta_2Cl_{10}(P_4S_{10})_2$ is isotypic with $Nb_2Cl_{10}(P_4S_{10})_2$, the lattice constants are a = 9.643(3), b = 10.963(3), c = 11.572(4) Å; α = 71.54(2), β = 68.11(2), γ = 67.61(2)°.

Keywords: Phosphorus sulphide; Niobium chloride; Tantalum chloride; Crystal structure; Raman spectroscopy

Introduction

The stabilisation of pnicogen-, chalcogen- and pnicogen chalcogenide molecules by metal halides has been studied intensively during the last years. Because of its structural flexibility, copper(I) iodide proved to be especially suited to act as a matrix for the synthesis of new molecules of group 5 and group 6 elements [1]. Several compounds like $(CuI)_3\beta$-P_4S_4 [2], $(CuI)_3\beta$-P_4Se_4 [3], $(CuI)_2P_8Se_3$ [4], and $(CuI)P_4Se_4$ [5] arose from these investigations. They contain neutral phosphorus chalcogenide molecular structures that are still unknown from the binary systems. For instance the hypothetical β-cage of P_4Se_4, which is structurally analogous to the As_4S_4 molecules in *pararealgar* [6], was found in $(CuI)_3\beta$-P_4Se_4 [3]. Two similar coordination compounds were found for $NbCl_5$. Inspired by the compounds $(NbCl_5)_2\beta$-P_4S_4 and $(NbCl_5)P_4Se_3$ [7] we carried out first experiments starting from Nb_2Cl_{10} and Ta_2Cl_{10}, respectively, to elucidate the existence of related compounds systematically. These studies should provide information about the coordination behaviour of a phosphorus chalcogenide cage where phosphorus is completely saturated by chalcogen (sulphur in this case) in presence of MCl_5 or M_2Cl_{10} (M = Nb, Ta) as prospective coordination partner. The compounds $M_2Cl_{10}(P_4S_{10})_2$ resulted, which can be considered as co-crystals of neutral P_4S_{10} and M_2Cl_{10} molecules.

* Prof. Dr. A. Pfitzner
Inst. f. Anorg. Chemie der Universität
Universitätsstr. 31
D-93040 Regensburg
E-mail: arno.pfitzner@chemie.uni-regensburg.de

Experimental

Synthesis

$Nb_2Cl_{10}(P_4S_{10})_2$ was obtained from the binary phases in organic solvents. P_4S_{10} was synthesised from phosphorus (Hoechst, ultra high grade) and sulphur (chempur, 99.999 %) by heating stoichiometric mixtures to 400 °C followed by slow cooling [8]. According to [7] 206 mg (0.46 mmol) of the sulphide P_4S_{10} and 500 mg (0.92 mmol) Nb_2Cl_{10} (HC Starck, 99.999 %) were filled under an argon atmosphere into a Schlenk flask and covered with 2 ml of dry CS_2 (Aldrich, >99 %) as well as 1.5 ml of dry *n*-hexane (Aldrich, >99 %). The mixture was kept at room temperature under an argon atmosphere. Small, red, moisture−sensitive crystals formed after several days.

$Ta_2Cl_{10}(P_4S_{10})_2$ was synthesised similarly using 664 mg (0.92 mmol) Ta_2Cl_{10} (strem, 99.9 %) and 206 mg (0.46 mmol) P_4S_{10}. The resulting pale yellow crystals are also moisture−sensitive.

Crystal structure determination

Suitable crystals for X-ray structure analysis were handled in an argon-filled glove box; they were isolated from the reactant mixture and filled into sealed glass capillaries to prevent decomposition due to the moisture sensitivity. Data collection was performed using a four-circle diffractometer Xcalibur S with MoK_α radiation. A numerical absorption correction of the intensities was applied. The structure was solved by direct methods and refined against F^2 with anisotropic displacement parameters for all atoms using the SHELX-97 programme package [9]. Table 1 summarises the results of

Table 1 Crystallographic data and details of the structure refinement for $Nb_2Cl_{10}(P_4S_{10})_2$.

Formula		$NbCl_5P_4S_{10}$
Molar mass in g·mol^{-1}		714.72
Crystal system, space group		triclinic, $P\bar{1}$ (No. 2)
Number of formula units	Z	2
Temperature in °C	T	293(2)
Lattice parameters in Å resp. °	a	9.577(2)
from single crystal data	b	10.894(2)
	c	11.477 (2)
	α	71.40(1)
	β	68.14(1)
	γ	67.58(1)
Cell volume in Å^3	V	1005.2(3)
Calculated density in g·cm^{-3}	ρ_{calc}	2.36
Crystal size in mm		0.20 × 0.19 × 0.11
Diffractometer		four-circle diffractometer (Xcalibur S, Oxford)
		graphite monochromator
		MoK_α radiation (λ = 0.71073 Å)
Range of data collection	2θ	7.0° − 50.6°
		$-11 \le h \le 8$
		$-13 \le k \le 12$
		$-13 \le l \le 12$
Absorption correction		numerical with optical description of the crystal shape [10]
Absorption coefficient in mm^{-1}	μ (MoK_α)	2.60
No. of reflections collected (independent)		6587 (3563)
	R_{int}, R_σ	0.044, 0.071
Structure solution		SHELXS 97 [9], direct methods
Structure refinement		SHELXL 97 [9], full-matrix least-squares method, refinement on F_o^2; anisotropic displacement parameters
No. of refined parameters		181
Residual electron density in e·Å^{-3}		+ 0.98 / − 0.44
	R_1 ($F_o > 4\ \sigma(F_o)$)	0.058
	R_1 (all F_o)	0.088
	wR_2 (all F_o)	0.132
	GooF	1.03
Weighting parameters	a, b	0.06, 0

the single crystal structure analysis of $Nb_2Cl_{10}(P_4S_{10})_2$. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666, e-mail: crysdata@fiz-karlsruhe.de) referring to number CSD-416095, name of the authors and citation of the paper.

$Ta_2Cl_{10}(P_4S_{10})_2$ was also analysed by X-ray diffraction. It is isotypic to the title compound and crystallises in the space group $P\bar{1}$ with a slightly enlarged unit cell (lattice parameters a = 9.643(3), b = 10.963(3), c = 11.572(4) Å; α = 71.54(2), β = 68.11(2), γ = 67.61(2)°). All crystals examined were systematically twinned and thus no satisfying structure refinement could be achieved so far.

Raman spectroscopy

Raman measurements were performed on a LabRam spectrometer (Jobin Yvon; single stage device with notch filter; HeNe laser, λ = 632.817 nm; CCD detection system). Single crystals of $Nb_2Cl_{10}(P_4S_{10})_2$ were analysed in various orientations.

Results and discussion

Crystal structure

$Nb_2Cl_{10}(P_4S_{10})_2$ consists of independent niobium pentachloride molecules and phosphorus sulphide molecules, see Figure 1a. The $NbCl_5$ molecules form dimers similar to both modifications of the binary metal halide, i.e., pairs of two distorted edge-sharing octahedra according to $(NbCl_{4/1}Cl_{2/2})_2$. The P_4S_{10} component of $Nb_2Cl_{10}(P_4S_{10})_2$ displays adamantane analogous cages which are structurally equal to those in P_4S_{10} and in P_4O_{10}. The packing of the molecules in the crystal can be described as a heavily distorted CaF_2 type, where Nb_2Cl_{10} molecules take the positions of calcium cations and P_4S_{10} molecules those of the fluoride anions, see Figure 1b. Atom coordinates and anisotropic displacement parameters of all atoms are given in Tables 2 and 3.

The bond distances and angles are summarised in Table 4. They agree with those of the binary starting materials within triple standard deviations. Since the phosphorus atoms in P_4S_{10} are saturated by sulphur there exist no interactions between niobium and phosphorus atoms, see Figure 2, contrary to the situation in adducts formed by $NbCl_5$ and phosphorus chalcogenides [7], where phosphorus lone electron pairs coordinate to niobium. In the case of $(NbCl_5)_2\beta$-P_4S_4 [7] two of the three basal phosphorus atoms coordinate to $NbCl_5$, in $(NbCl_5)P_4Se_3$ [7] one basal phosphorus atom of the P_4Se_3 cage is coordinated to $NbCl_5$. In these compounds niobium pentachloride forms square pyramids. Including the attached phosphorus atom an octahedron results as coordination polyhedron of niobium. One might also expect a coordination of niobium to sulphur of the P_4S_{10} cage which is for example found in the adduct

Table 2 Atom coordinates and equivalent isotropic displacement parameters U_{eq} [a] of $Nb_2Cl_{10}(P_4S_{10})_2$

Atom	*x*	*y*	*z*	U_{eq} in Å^2
P(1)	0.0108(2)	0.3282(2)	0.7627(2)	0.0284(5)
P(2)	0.3083(2)	0.3565(2)	0.8423(2)	0.0275(5)
P(3)	0.3858(2)	0.2705(2)	0.5579(2)	0.0277(5)
P(4)	0.3034(2)	0.0435(2)	0.8402(2)	0.0257(4)
S(1)	−0.2086(2)	0.4004(2)	0.7733(2)	0.0435(6)
S(2)	0.0673(2)	0.4341(2)	0.8548(2)	0.0302(5)
S(3)	0.1456(2)	0.3497(2)	0.5693(2)	0.0298(5)
S(4)	0.0630(2)	0.1220(2)	0.8519(2)	0.0297(5)
S(5)	0.3573(3)	0.4534(2)	0.9271(2)	0.0434(6)
S(6)	0.4432(2)	0.3767(2)	0.6491(2)	0.0308(5)
S(7)	0.3585(2)	0.1504(2)	0.9318(2)	0.0306(5)
S(8)	0.5057(3)	0.2902(2)	0.3812(2)	0.0403(5)
S(9)	0.4370(2)	0.0647(2)	0.6468(2)	0.0292(5)
S(10)	0.3499(3)	−0.1439(2)	0.9237(2)	0.0390(5)
Nb(1)	0.04433(8)	0.13346(7)	0.33697(7)	0.0295(2)
Cl(1)	0.1414(2)	0.0130(2)	0.5361(2)	0.0294(4)
Cl(2)	0.2122(2)	−0.0561(2)	0.2561(2)	0.0394(5)
Cl(3)	−0.0772(3)	0.2154(2)	0.1814(2)	0.0440(6)
Cl(4)	−0.1350(2)	0.2905(2)	0.4578(2)	0.0400(5)
Cl(5)	0.2268(3)	0.2432(2)	0.2590(2)	0.0443(5)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 3 Tensor coefficients U_{ij} (in Å^2) [a)] of the anisotropic displacement parameters in $Nb_2Cl_{10}(P_4S_{10})_2$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	0.025(2)	0.027(2)	0.032(2)	−0.0046(9)	−0.0094(9)	−0.007(1)
P(2)	0.030(2)	0.029(2)	0.026(2)	−0.010(1)	−0.0087(9)	−0.0062(9)
P(3)	0.029(2)	0.029(2)	0.024(2)	−0.009(1)	−0.0076(9)	−0.0045(9)
P(4)	0.025(1)	0.023(2)	0.026(2)	−0.0050(9)	−0.0076(9)	−0.0047(9)
S(1)	0.027(2)	0.045(2)	0.056(2)	−0.004(2)	−0.013(2)	−0.014(2)
S(2)	0.029(2)	0.028(2)	0.035(2)	−0.0053(9)	−0.0082(9)	−0.014(1)
S(3)	0.028(1)	0.031(2)	0.027(2)	−0.0064(9)	−0.0101(9)	−0.0027(9)
S(4)	0.026(1)	0.027(2)	0.036(2)	−0.0091(9)	−0.0097(9)	−0.0028(9)
S(5)	0.050(2)	0.047(2)	0.043(2)	−0.016(2)	−0.015(2)	−0.018(2)
S(6)	0.034(2)	0.034(2)	0.028(2)	−0.018(1)	−0.0056(9)	−0.0073(9)
S(7)	0.036(2)	0.032(2)	0.026(2)	−0.010(1)	−0.0143(9)	−0.0023(9)
S(8)	0.044(2)	0.046(2)	0.026(2)	−0.016(2)	−0.004(1)	−0.005(1)
S(9)	0.031(2)	0.026(2)	0.027(2)	−0.0062(9)	−0.0060(9)	−0.0062(9)
S(10)	0.044(2)	0.030(2)	0.039(2)	−0.011(1)	−0.015(2)	0.002(1)
Nb(1)	0.0305(4)	0.0284(4)	0.0280(4)	−0.0088(3)	−0.0075(3)	−0.0046(3)
Cl(1)	0.029(1)	0.032(1)	0.029(1)	−0.0125(8)	−0.0106(8)	−0.0028(8)
Cl(2)	0.036(1)	0.039(1)	0.037(1)	−0.006(1)	−0.0036(9)	−0.015(1)
Cl(3)	0.049(1)	0.047(1)	0.040(1)	−0.012(1)	−0.023(1)	−0.005(1)
Cl(4)	0.040(1)	0.034(1)	0.043(1)	−0.005(1)	−0.010(1)	−0.012(1)
Cl(5)	0.040(1)	0.046(1)	0.050(1)	−0.024(1)	−0.006(1)	−0.006(1)

[a)] Coefficients U_{ij} of the anisotropic displacement factor tensor of the atoms are defined by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$.

compound $(NbCl_5)Ph_3PS$ [11]. Therein, this apparently results from a lack of free bonding sites at phosphorus. In the case of $Nb_2Cl_{10}(P_4S_{10})_2$ rather large complexes would form when niobium coordinates the terminal sulphur atoms. Certainly such complexes cannot be packed efficiently and the dimerisation of $NbCl_5$ is favoured.

Furthermore, it seems worth mentioning that no fragmentation of the P_4S_{10} cages takes place. Such fragmentations are observed in several reactions of transition metal complexes with phosphorus sulphide cages, e.g. in the reaction of $[RhCl(1,5\text{-cyclooctadiene})]_2$ and *triphos* ($CH_3C(CH_2PPh_2)_3$) with P_4S_3 [12]. A basal phosphorus atom of the P_4S_3 cage is replaced by rhodium forming [*triphos*$Rh(P_3S_3)$]. Such a cleavage of bonds within the phosphorus sulphide framework and the generation of adducts consisting of niobium pentachloride and smaller phosphorus sulphide cages or even the formation of phosphorus chlorides and niobium sulphides is not to be ruled out when applying less mild conditions to the title compound.

Table 4a Bond distances in $Nb_2Cl_{10}(P_4S_{10})_2$

Bond		Distance in Å	Bond		Distance in Å
P(1)	- S(1)	1.913(3)	P(2)	- S(2)	2.099(3)
	- S(2)	2.102(3)		- S(5)	1.913(3)
	- S(3)	2.101(3)		- S(6)	2.099(3)
	- S(4)	2.098(3)		- S(7)	2.098(3)
P(3)	- S(3)	2.095(3)	P(4)	- S(4)	2.095(3)
	- S(6)	2.103(3)		- S(7)	2.098(3)
	- S(8)	1.911(3)		- S(9)	2.098(3)
	- S(9)	2.094(3)		- S(10)	1.914(3)
Nb(1)	- Cl(1)	2.559(2)	Nb(1)	- Cl(3)	2.253(2)
	- Cl(1^i)	2.566(2)		- Cl(4)	2.302(2)
	- Cl(2)	2.300(2)		- Cl(5)	2.244(2)

(*i*): $-x, -y, -z$

Table 4b Comparison of the mean bond distances of $Nb_2Cl_{10}(P_4S_{10})_2$, $(NbCl_5)_2\beta$-P_4S_4, and the binary starting materials Nb_2Cl_{10} and P_4S_{10}

Mean distance in Å for the bonds	$Nb_2Cl_{10}(P_4S_{10})_2$	P_4S_{10} [13] and α- and β-Nb_2Cl_{10} [14, 15]	$(NbCl_5)_2\beta$-P_4S_4 [7]
P - S(bridging)	2.10(1)	2.10(2)	2.11(1)
P - S(terminal)	1.91(1)	1.90(2)	−
Nb - Cl(bridging)	2.56(1)	2.56(2) α, 2.57(1) β	−
Nb - Cl(terminal)	2.30(1); 2.25(1)	2.30(4) α, 2.29(1) β; 2.25(2) α, 2.25(1) β	2.32(1) 2.25(1)

Raman spectroscopy

Vibrational spectroscopy is an excellent method to estimate the bonding interaction in adduct compounds. For instance, the resonances of $[SbS_3^{3-}]$ vibrations in β-Cu_3SbS_3 range from about 280 to 330 cm^{-1} whereas the corresponding resonances for $(CuI)_2Cu_3SbS_3$ are found between about 330 and 370 cm^{-1} [16]. This shift is attributed to the different coordination spheres of antimony atoms with further sulphur atoms of surrounding thioantimonate units in β-Cu_3SbS_3 on the one hand and the separation of these units in $(CuI)_2Cu_3SbS_3$ on the other hand. Raman spectra of crystalline $Nb_2Cl_{10}(P_4S_{10})_2$ were recorded in order to analyse the bonding interactions between the building units. The Raman spectrum of the title compound is shown in Figure 3. All observed bands can be attributed to vibration modes of the independent P_4S_{10} and Nb_2Cl_{10} molecules and no additional modes are observed. They cover a frequency range from about 100 to 720 cm^{-1}, with bands of the P_4S_{10} cages between 110 and 720 cm^{-1} and bands of Nb_2Cl_{10} between 100 und 420 cm^{-1}. The Raman bands of specific modes of the different molecules in the structure were assigned by comparison with reported data of the binary compounds [17], see Figure 3. The deviations of the frequencies of $Nb_2Cl_{10}(P_4S_{10})_2$ and of the binaries are less than 5 cm^{-1} for all bands. Of course the environment of the

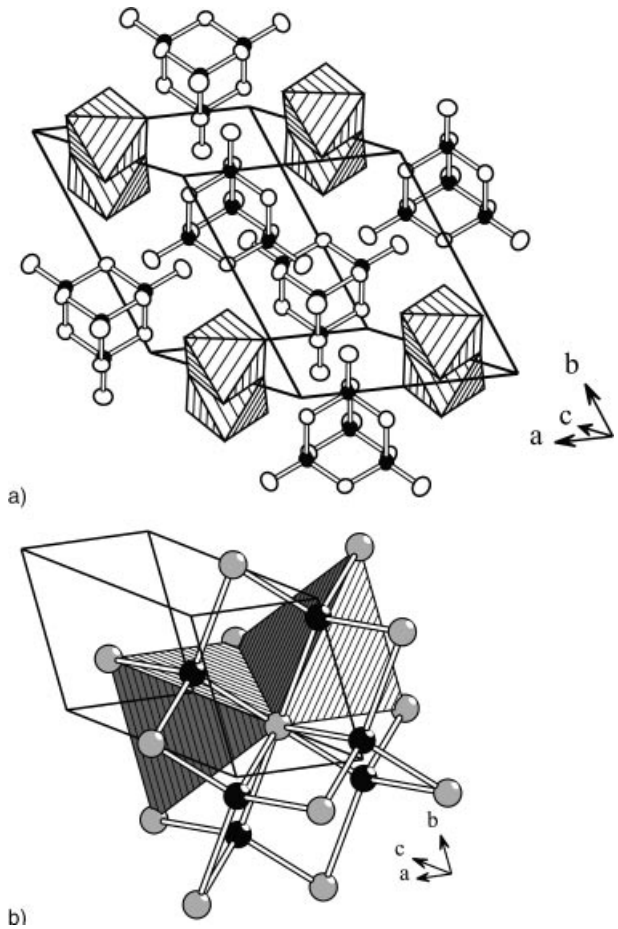

Figure 1 a) Section of the crystal structure of $Nb_2Cl_{10}(P_4S_{10})_2$. Black: phosphorus; white: sulphur; hatched double octahedra: Nb_2Cl_{10}. b) Arrangement of the centres of Nb_2Cl_{10} (grey) and of P_4S_{10} (black) showing the relation to the CaF_2 structure type.

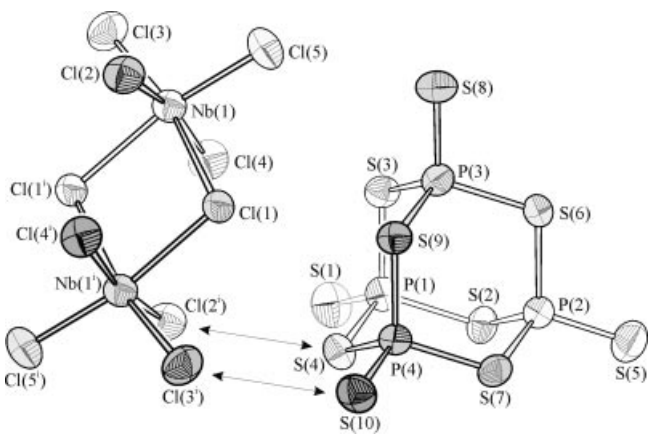

Figure 2 Adjacent molecules Nb_2Cl_{10} (left side; (*i*): $-x, -y, -z$) and P_4S_{10} (right side). Ellipsoids enclose 70 % probability for atomic displacement. Arrows indicate shortest distances between the molecules (3.66 Å), being slightly longer than the van der Waals distance (3.6 Å) for the considered atoms.

molecules in the binary phases differs from the environment of those in the title compound. The minimum intermolecular (non-bonding) distance of sulphur atoms in P_4S_{10} is 3.56 Å and the minimum intermolecular (non-bonding) distance of chlorine atoms in α- and β-Nb_2Cl_{10} is 3.63 Å. In the co-crystal $Nb_2Cl_{10}(P_4S_{10})_2$ we observe a minimum intermolecular (non-bonding) distance between sulphur and chlorine atoms of 3.66 Å. It is quite obvious that this fact does not influence molecular vibration frequencies. This emphasises the "independence" of both kinds of molecules once more.

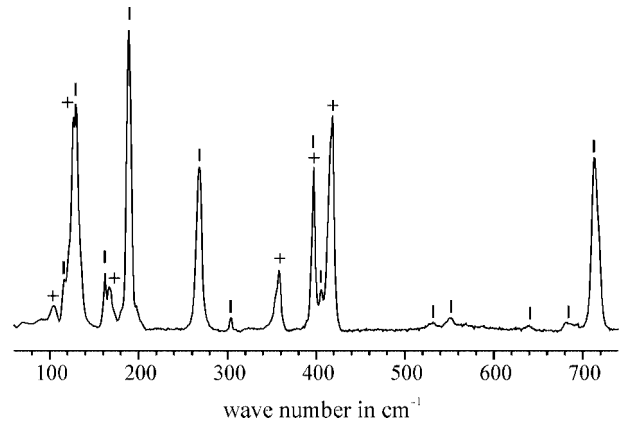

Figure 3 Raman spectrum of $Nb_2Cl_{10}(P_4S_{10})_2$ (excitation wavelength 633 nm). P_4S_{10} bands are marked with "|" and Nb_2Cl_{10} bands with " + ".

Conclusion

There are exclusively van der Waals interactions present between the constituting molecules in $Nb_2Cl_{10}(P_4S_{10})_2$. A similar situation is to be found in WCl_6S_8 [18], a co-crystal consisting of single sulphur rings S_8 and WCl_6 octahedra. A coordination of sulphur atoms of the phosphorus sulphide species to niobium pentachloride does not occur here. This is contrary to chemically related compounds [7] and numerous other compounds of phosphorus chalcogenide cages and transition metal complexes that are described in the literature, where different coordination types including several fragmentation possibilities of the cages are found. E.g., in Ag^+-P_4S_3 complexes with weakly coordinating counterions [19] the coordination of the cage to the metal is realised via the apical or basal phosphorus atoms as well as via bridging sulphur atoms.

It is still an open question under which conditions these coordination compounds form − with or without fragmentation or bond cleavage −, and − in case of their formation − which atoms interact and why. Detailed investigations to the discussed problems will follow.

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References

[1] A. Pfitzner, *Chem. Eur. J.* **2000**, *6*, 1891.
[2] S. Reiser, G. Brunklaus, J. H. Hoy, J. C. C. Chan, H. Eckert, A. Pfitzner, *Chem. Eur. J.* **2002**, *8*, 4228.
[3] A. Pfitzner, S. Reiser, *Inorg. Chem.* **1999**, *38*, 2451.
[4] A. Pfitzner, S. Reiser, T. Nilges, *Angew. Chem.* **2000**, *112*, 4328; *Angew. Chem. Int. Ed.* **2000**, *39*, 4160.
[5] A. Pfitzner, S. Reiser, H.-J. Deiseroth, *Z. Anorg. Allg. Chem.* **1999**, *625*, 2196.
[6] a) A. Kutoglu, *Z. Anorg. Allg. Chem.* **1976**, *419*, 176; b) P. Bonazzi, S. Menchetti, G. Pratesi, *Am. Mineral.* **1995**, *80*, 400.
[7] H. Nowottnick, K. Stumpf, R. Blachnik, H. Reuter, *Z. Anorg. Allg. Chem.* **1999**, *625*, 693.
[8] R. Blachnik, A. Hoppe, *Z. Anorg. Allg. Chem.* **1979**, *457*, 91.
[9] G. M. Sheldrick, SHELX-97, Program for Crystal Structure Determination, University of Göttingen **1997**.
[10] X-RED 1.22, Program for data reduction, STOE & Cie, Darmstadt, Germany **2001**.
[11] K. Stumpf, R. Blachnik, G. Roth, G. Kastner, *Z. Kristallogr. NCS* **2000**, *215*, 589.
[12] M. Di Vaira, M. Peruzzini, P. Stoppioni, *J. Chem. Soc., Chem. Commun.* **1983**, 903.
[13] R. Blachnik, J. Matthiesen, A. Müller, H. Nowottnick, H. Reuter, *Z. Kristallogr.* **1998**, *213*, 233.
[14] W. Hönle, H. G. von Schnering, *Z. Kristallogr.* **1990**, *191*, 139.
[15] F. A. Cotton, P. A. Kibala, M. Matusz, R. B. W. Sandor, *Acta Crystallogr.* **1991**, *C47*, 2435.
[16] A. Pfitzner, *Chem. Eur. J.* **1997**, *3*, 2032.
[17] a) I. R. Beattie, T. R. Gilson, G. A. Ozin, *J. Chem. Soc. A* **1968**, 2765; b) M. Somer, W. Bues, W. Brockner, *Z. Naturforsch.* **1983**, *38a*, 163; c) J. O. Jensen, D. Zeroka, *J. Mol. Struct. (Theochem)* **1999**, *487*, 267; d) S. J. Cyvin, H. Hovdan, W. Brockner, *J. Inorg. Nucl. Chem.* **1975**, *37*, 1905; e) R. D. Werder, R. A. Frey, H. H. Günthard, *J. Chem. Phys.* **1967**, *47*, 4159.
[18] F. A. Cotton, P. A. Kibala, R. B. W. Sandor, *Acta Crystallogr.* **1989**, *C45*, 1287.
[19] A. Adolf, M. Gonsior, I. Krossing, *J. Am. Chem. Soc.* **2002**, *124*, 7111.

